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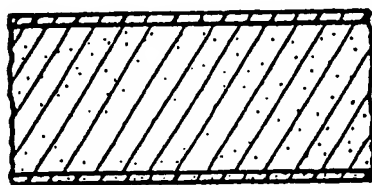
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(54) Title: URETHANE-MODIFIED BITUMEN SHEET MATERIAL AND METHOD FOR PROTECTIVE MOISTURE BARRIER

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2



12~LDPE FILM  
14~URETHANE-MODIFIED  
BITUMEN  
16~RELEASABLE  
CASTING FILM

(57) Abstract

A modified bitumen sheet material (12) and method for a protective moisture barrier, particularly for masonry surfaces (42). The sheet material has a bitumen layer (14) modified by the addition of a minor amount of a long-chain polybutadiene-isocyanate urethane polymer and optionally, a modifying amount of hydrocarbon oil to provide stable, non-flow and selected tackified surface properties to the bitumen layer (14). The sheet material (12) includes a releasable casting paper film (16) on one surface of the bitumen layer (14), to be removed prior to use, and a cross-linked polyethylene film (12) bonded to the other outer surface of the bitumen layer (14) as a handling or moisture barrier sheet. The sheet material (12) is prepared by casting the hot, melted bitumen as a layer (14) onto a casting paper sheet (16) and applying the outer film to the exposed bitumen surface to bond to the top surface.

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## DESCRIPTION

Urethane-Modified Bitumen Sheet Material  
and Method for Protective Moisture BarrierBackground of the Invention

5 Asphalt is a solid or viscous, typically semisolid, mixture of hydrocarbons which are amorphous, and the predominant constituents of asphalt are bitumens derived from refinery petroleum. Asphalts and/or bitumens are typically employed for paving, road coatings, roofings,  
10 sealing and also for carpet backing, such as a bitumen-backed carpet tile.

Asphalt or bitumen has been employed as a backing layer for carpet material. Such bitumen employed as a backing layer has been modified by the addition of various polymers,  
15 for example, styrene-butadiene-styrene block copolymers as well as mixtures of high and low density polyethylene polymers, and by urethane polymers as described more particularly in U.S. Patent 5,096,764, issued March 17, 1992, hereby incorporated by reference. Bitumen used as a  
20 backing layer for a carpet material has been modified by employing therein a urethane reaction product composed of a hydroxyl-terminated, long-chain diene hydrocarbon and a polyisocyanate to provide a carpet material which is heat stable during a wet steam process printing operation. The  
25 liquid hydroxyl-terminated homopolymers of butadiene employed as the modifying polymers in the bitumen carpet backing layer are commercially sold as Poly-BD® liquid resins (a trademark of ELF-Atochem SA of Hauts-de-Seine, France), and their use with various polymers and components  
30 are described in an advertising brochure "Poly bd® resins In Urethane Elastomers", also hereby incorporated by reference.

Asphalt or bitumen has a primary use as a moisture barrier for masonry, such as poured concrete, in the construction of commercial and residential buildings wherein  
35 a bitumen coating is typically applied to the exterior wall after the concrete foundation has been poured to prevent the

penetration of moisture. The use of bitumen coatings as a moisture-protective barrier by itself is difficult, since bitumen tends to be too fluid, therefore usually requiring a backing and also a filler, such as a modified polymer, like the styrene-butadiene-styrene, in order to stiffen the bitumen as a moisture barrier. However, bitumen even with a filler and a styrene-butadiene-styrene copolymer is not satisfactory at normal operating ranges, since at the high temperature end of the application of the bitumen as a moisture barrier, say for example 80°F to 110°F, the bitumen is too fluid, while at low temperatures, the bitumen exhibits diminished surface tackiness, for example, in the 10°F to 30°F range, so that the bitumen does not stick to the masonry it is designed to protect.

Therefore, it is desirable to provide for a new, improved, modified bitumen composition sheet material and method as a moisture barrier in which the modified bitumen sheet material may be employed over a range of temperatures with satisfactory characteristics, such as preventing the passage of moisture, tackiness and flexibility.

#### Summary of the Invention

The invention concerns a modified bitumen sheet material and method as a moisture barrier. In particular, the invention is directed to a polybutadiene urethane-polymer-modified, bitumen-containing sheet material and method as a moisture barrier for concrete structures.

The invention is directed to a modified bitumen sheet material, adapted particularly for use as a moisture barrier for masonry, such as poured concrete, and which sheet material comprises a modified bitumen layer, which bitumen layer comprises bitumen (or asphalt used interchangeably with bitumen), optionally a filler material, such as an inert, low cost, particulate filler, optionally a tackifier agent and a minor modifying amount of a urethane polymer, the urethane polymer prepared by the reaction of a polyisocyanate, such as an aromatic diisocyanate, with a long-chain polydiene hydrocarbon, such as a polybutadiene,

having isocyanate-reactive terminal groups, particularly hydroxyl terminal groups, which react with the polyisocyanate. The urethane-modified bitumen layer is selected in composition to impart stable, non-flow  
5 properties to the bitumen layer and also a selected degree of surface tackiness to the bitumen layer over a selected general use temperature range in which the bitumen layer is employed as a moisture barrier.

The sheet material includes a thin, polymer film,  
10 particularly, for example, a thin film of non-heat-shrinkable film, such as an oriented olefinic resin, like a polyethylene or a polyester, for example, from about 0.5 to 5 mils in thickness on one surface of the bitumen layer, and also includes a thin, releasable film on the other surface  
15 of the bitumen layer, such as a paper casting sheet having a surface treatment, like a silicone coating, which provides for the releasable film sheet to be easily removed prior to use of the sheet material to expose the tackified surface of the bitumen layer for application to a wall surface of the  
20 masonry to be protected.

Optionally, but preferably, the bitumen composition should contain a modifying amount of a tackifier agent which is compatible with the urethane-modified bitumen composition and which permits the adjustment of the degree of tackiness  
25 to the urethane-bitumen composition. Suitable tackifier agents would include waxes, resins and oils. In particular, petroleum or petroleum-derived mineral oil, such as aliphatic, aromatic or mixed base hydrocarbon oil has been discovered to be a satisfactory tackifier agent with the  
30 urethane-bitumen composition, generally in the range of 0% to 30%, e.g. 10% to 25%, by weight of the urethane-bitumen composition. Generally, the tackifier agent is added to the bitumen and filler where a multiple vessel preparation system is used.

35 The composition of the bitumen layer may vary as desired as to the type and nature of the bitumen, of the fillers, and of the modifying urethane polymer employed in

order to provide the desirable balance of properties of both being flexible and stable and having a tacky surface depending upon the particular usage and climate on application to which the bitumen sheet material is employed.

- 5 Thus, the modified bitumen sheet material may be formulated for example for use at various particular temperature ranges or may be formulated for use as a general residential and commercial building moisture barrier sheet material. The sheet material is provided in roll form for application of
- 10 the exposed tacky surface of the bitumen layer to the exposed exterior, or even interior, surface of a surface, such as a poured concrete wall, to provide for an effective barrier layer. It is desirable to provide for a modified bitumen sheet material which exhibits desirable properties,
- 15 that is, surface tackiness on the exposed bitumen layer surface after removal of the releasable film, as well as flexibility and stability over a range of about 10°F to 120°F, and more typically, 25°F to 100°F, which would cover
- 
- 20 most moderate climatic operations. The desired flexibility should be such as to permit the sheet material to be manufactured, employed and transported to the site typically in roll form, so that it may be easily unrolled, cut to desired lengths for application and then applied to a surface, typically a vertical concrete wall surface, for
- 25 example, about the exterior surface of a poured foundation. The bitumen exposed surface layer should be sufficiently tacky when the releasable film is removed to permit the exposed bitumen layer surface to adhere to the masonry wall surface, at least for a sufficient time to permit the back
- 30 filling of earth against the foundation wall or for the application of other wall surfaces or other coating or treatment applications, where desired, to the moisture barrier sheet.

- 35 The bitumen or asphalt employed as the primary constituent may represent straight run, cut back asphalt, low asphaltene bitumen, propane deactivated bitumen or blown asphalt and may vary in penetration properties, but

typically ranging from about 10 to 100, more typically 30 to 80, in penetration value. The filler material employed may vary and generally is an inert-type filler material, either fibrous or particulate, and more particularly, comprises  
5 calcium carbonate, talc, clay, diatomaceous earth or other low cost-type filler material which is easily dispersed into the bitumen in order to stiffen the bitumen and to lower the cost of the resulting bitumen layer. However, calcium carbonate is the preferred particulate material to be  
10 employed in fine particle size of less than about an average size of 100  $\mu\text{m}$ , and typically less than 20  $\mu\text{m}$ , in a range of at least 6% by weight of the bitumen layer, and generally ranging from about 0 to 40 weight percent, but more typically from 5 to 25 weight percent of the bitumen  
15 composition.

The urethane polymer is a reaction product generally reacted *in situ* in the melted bitumen by the addition of polyisocyanate and the addition of the long-chain diene polymer, typically in the presence of a urethane catalyst  
20 curing system. The bitumen and the components are mixed to provide for an *in situ* reaction urethane polymer, wherein the components of the urethane polymer are dispersed within the hot bitumen forming an interpenetrating polymer network (IPN) prior to the formation, i.e. casting or pouring, of  
25 the hot-melt bitumen composition onto a releasable film, usually supported on a movable belt, to form the sheet material. The long-chain diene hydrocarbon polymer employed has terminal groups, more particularly, hydroxyl terminal groups, or amine-type terminal groups or any other  
30 isocyanate reaction-type groups which would permit the long-chain diene, i.e.  $\text{C}_4\text{-C}_6$ , hydrocarbon polymer to provide for a desirable reaction with the isocyanate groups. One particular long-chain diene polymer employed comprises a homopolymer of polybutadiene, commercially known as Poly-BD®  
35 resin, having a hydroxyl functionality ranging from about 2.2 to about 2.6, which is particularly reactive with aromatic diisocyanates, and which polymer has primarily

terminal hydroxyl groups of the allylic type. While the bitumen composed of a reasonably high molecular weight carbon chain typically has limited compatibility with the isocyanate, polybutadiene or low weight polybutadiene-urethane polymer, the components are easily admixed. The use of a long-chain diene hydrocarbon with terminal isocyanate reactive groups exhibits the most compatibility with the non-polar bitumen. The polyurethane polymer provides for the formation of a cross-linked, interpenetrating urethane polymer network through the normally thermoplastic bitumen to provide a urethane-modified bitumen which will no longer flow, i.e. is stable but will retain tacky properties. The isocyanate is chemically bonded to the bitumen by the isocyanate-reactive groups, like amine groups, on the bitumen.

While in one preferred embodiment, the isocyanate and the long-chain hydrocarbon are reacted *in situ* with the hot bitumen and then filler material added and dispersed therein, it is also recognized that the urethane polymer can be separately reacted, for example, as a prepolymer, and then dispersed by mixing or a dispersion mill into the bitumen. The reaction may be carried out employing varying amounts of the isocyanate and the long-chain polydiene hydrocarbon, but typically the reaction is carried out using a stoichiometric amount or with a slight excess of the polyisocyanate, i.e. in an equivalency ratio of about 1.0 to 1.1. It is recognized that the reactive long-chain poly C<sub>4</sub>-C<sub>8</sub> hydrocarbon, i.e. polybutadiene, may be used in less than stoichiometric amounts and also used in combination and with mixtures of other polyols, amines or amine polyol compounds reactive with isocyanates or isocyanate prepolymers containing polyols prepared with these compounds for admixture with the bitumen, such compounds and prepolymers known and used in the urethane field to produce urethane polymers. The urethane polymers so produced provide desired modified polyol or amine polyol-hydroxy polybutadiene-isocyanate reaction products as a modifying agent for the



bitumen. Suitable polyols would include, but not be limited to: C<sub>2</sub>-C<sub>10</sub> polyols, like butane diols, hexane diols, trimethylolpropane, propylene glycol, or polyethylene polyols prepared using C<sub>2</sub>-C<sub>4</sub> oxide, like ethylene and propylene oxides and halogenated oxides.

As set forth, the nature and amount of the various ingredients in the bitumen layer may be varied as desired for desired properties within the sheet material, for example and not in limitation thereof, a bitumen composition may comprise about 100 parts bitumen (straight run or oxidized) with 10 to 70 parts of a particulate filler, like calcium carbonate, and the urethane polymer in an amount of about 2% to 25% by weight of the composition, more typically ranging from about 6% to 18% with the polymer prepared with a hydroxy-terminated polybutadiene and reacted with a minor amount of an MDI diisocyanate in the presence of a catalyst system. The reaction usually is carried out in the presence of a urethane curing system which may include, for example, an organo-metal compound alone or in combination with other catalysts with various amines as accelerators, such as for example, but not limited to a dialkyl metal, e.g. tin, di-fatty acid, and more particularly, a di-butyl tin dilaurate catalyst. The components are brought together in a heater-mixer with the bitumen and heated to about 180°F or higher, such 200°F to 300°F, to provide the urethane polymer bitumen composition.

The releasable sheet material comprises strippable or releasable casting paper or other type film which does not adhere to the surface of the bitumen layer, typically, a thin casting paper having a silicone coating thereon of about 1 to 5 mils in thickness and typically, 2 to 4 mils, and upon which the hot melt, modified, urethane polymer bitumen composition is cast and formed into a bitumen layer by a casting knife or roller operation, and then permitted to cool on the releasable paper. The releasable paper is easily stripped off in use, usually just prior to use as a moisture barrier layer, to expose the tacky surface of the

bitumen layer for pressing against a concrete wall or other surface.

The thin, outer film or other film employed may vary in composition and thickness and a wide variety of polymer layers used, either in single or double layers or as polymer-metal foil layers. The outer film may be used as a moisture barrier film; however, this outer film need not be a moisture barrier-type film, but is employed primarily to allow handling of the moisture-barrier, tacky bitumen layer. However, in particular, it is desirable to use an olefinic-type resin, typically ranging from 1 to 10 mils in thickness, for example, 1 to 5 mils, and generally of a polyethylene, thin film material, which is sufficiently stable at the melting point or the bitumen application temperature of the urethane-modified bitumen layer, so that it will not shrink or change characteristics. Thus, for example, particularly preferred are cross-linked-type olefinic resins and more particularly, a cross-linked, low density polyethylene film which will not shrink at the casting temperatures of a hot bitumen layer formation and which adheres to the bitumen layer.

The sheet material may be prepared by charging a heated mixing vessel with the bitumen, filler, curing system, long-chain polymer, polyisocyanate and other additives as desired, which may include stabilizers, surfactants, dispersants, pigments, dyes, tackifiers, other polymers and resins, waxes and the like, and the admixture heated and mixed to provide for the *in situ* reaction of the polyisocyanate and the hydrocarbon to provide for a urethane-modified bitumen. All the components need not be charged into a single heater-mixer; rather, in a preferred embodiment, one vessel will contain the hydroxy-terminated polybutadiene and the selected curing agents and other additives, the bitumen and filler heated and premixed in a second vessel and the polyisocyanate in a third vessel. The mixed components of the first and second vessel and the isocyanate in the third vessel may then be mixed in an

injection nozzle at the point of dispensing and pouring the mixed components onto the releasable film supported on a conveyor belt. Where a single heater-mixer vessel is used, the filler would be dispersed into the hot, melted bitumen prior to the addition of the curing system, the reactive, long-chain polydiene hydrocarbon and the polyisocyanate, then all components mixed and then dispersed to form a urethane-modified bitumen layer.

The hot bitumen composition is injected or cast onto a releasable film to form a bitumen layer, such as with the employment of a casting knife, to form a layer of moisture-barrier bitumen on the releasable film which may vary in thickness, but for example may range from about 30 to 150 mils, and more typically 40 to 100 mils in thickness. After the applying of the bitumen layer, the thin moisture barrier layer is gently pressed or laid on the top surface of the hot melt bitumen layer, the bitumen then permitted to cool or is cooled by the use of water-cooled plates usually beneath the belt, and then the resulting flexible sheet material rolled up in roll form for subsequent packaging and use in the field.

In use, the rolled up bitumen sheet material is transported to a construction or use site, and the sheet material cut to the desired lengths. The releasable casting film material is removed to expose the tackified surface, and the tacky surface then placed, i.e. pressed, against the masonry or other surface it is designed to protect, and held in place by the tacky nature of the exposed surface of the bitumen layer. The sheet material may be employed as adjacent sheet materials or the adjacent sheet materials may be overlapped as desired, and may further be spray coated by other polymers or used with other sheet material laid thereover or back filled of earth in whole or part as desired. The sheet material provides an effective, flexible, tackified, stabilized moisture barrier and method which may be employed not only on masonry surfaces, but also in a wide variety of applications wherein desirable

protective barrier properties are required across a desired temperature range.

The invention will be described for the purposes of illustration only in connection with certain, specific  
5 illustrated embodiments; however, it is recognized that those persons skilled in the art may make various modifications, changes, additions and improvements to the illustrated embodiments, without departing from the spirit and scope of the invention.

10 Brief Description of the Drawings

Fig. 1 represents an enlarged, cross-sectional view of the sheet material of the invention.

Fig. 2 is a schematic, illustrative process for producing the sheet material of Fig. 1.

15 Fig. 3 is an illustrative, schematic drawing of the application of the sheet material of Fig. 1 to a masonry surface.

Description of the Embodiments

Fig. 1 shows a moisture barrier sheet material 10  
20 having a urethane-modified bitumen layer 14 of 40 to 80 mils, a releasable, non-stick casting paper 16 of 1 to 2 mils and an outer handling film composed of low density, cross-linked, heat stable to 160°F polyethylene film 12.

Fig. 2 shows a process 20 for manufacturing the sheet  
25 material 10 employing heated mixing vessels 22, 30 and 32 wherein the bitumen and filler calcium carbonate are heated in vessel 30 to about 180°F to 270°F. The other vessels 32 and 22 contain the other components, and all components are fed through lines 34, 36 and 38 to a mixing-injection nozzle  
30 50 to admix and inject the polymer-bitumen composition onto the top surface of release paper 16. The urethane polymer is formed *in situ* in the nozzle 50. The hot, melted, injected bitumen composition is cast as layer of 40 to 80 mils in thickness by a knife 26 on the release surface of  
35 casting paper 16 supported on an endless stainless steel or, non-stick fluorocarbon or other type conveyor belt 24. A low density polyethylene barrier film 12 is then fed from a

roll and pressed onto the hot, exposed surface of the bitumen cast layer to adhere to the cooled bitumen layer. The bitumen layer is cooled by water cooling plates 28 beneath the conveyor belt 24, and the resulting product  
5 placed in roll form.

Fig. 3 shows a concrete wall protection system 40 with a poured, vertical, concrete foundation wall 42 with cast pieces of the sheet material 10 with casting paper 16 removed and the exposed tacky surface adhering to the  
10 concrete surface with earth 44 placed against a portion of the previous attached, secured sheet material 12 and 14.

#### Example I

The following bitumen-asphalt composition formula was prepared. The first five components are added to and mixed  
15 with asphalt at 250°F, the temperature adjusted to 230°F before adding the catalyst.

Asphalt-bitumen	350 grams (straight run hydrocarbon)
Oil	54
20 CaCO <sub>3</sub>	70
Poly BD®	65.5 (hydroxy-terminated polybutadiene)
(MDI) Isocyanate	8.2
Catalyst	<u>0.1</u> (dibutyl tin di-laurate)
25 Total	547.8 grams

The hot composition is poured directly onto release film supported on a belt and cures adequately after leveling to roll on line.

#### Example II

30 The example shows the effect of cure time on the amount of catalyst present in the mixture.

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Asphalt	21.0 gr	21.0	21.0	21.0
Oil	3.2	3.2	3.2	3.2
35 CaCO <sub>3</sub>	4.2	4.2	4.2	4.2
Poly BD®	3.9	3.9	3.9	3.9
Isocyanate	0.49	0.49	0.49	0.49
Catalyst	0.003	0.006	0.012	0.024
Cure Time	30 min	10 min	5 min	1 min

40 The optimum cure time is about 1/2 to 10 minutes, depending upon the time required to cast the composition, form a coating layer on the release film and apply a top

cover of the barrier film. The cure time may vary depending upon the amount of catalyst, as illustrated, and also may vary depending upon the type of catalyst or combination of catalysts used.

### 5 Example III

This example shows the effect on cold tack and fluidity at 100°F by varying the amount of oil. Tack is determined empirically by finger test against the composition surface, while fluidity is determined empirically by applying the composition to a vertical wall surface and observing downward movement with time; however, other tests of tack and fluidity may be used.

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
15 Asphalt	73.8 gr	73.8	73.8	73.8	73.8
Oil	11.4	15.0	20.0	25.0	30.0
CaCO <sub>3</sub>	14.8	14.8	14.8	14.8	14.8
Poly BD®	15.0	15.0	15.0	15.0	15.0
Isocyanate	1.88	1.88	1.88	1.88	1.88
Catalyst	0.1	0.1	0.1	0.1	0.1
20 Tack (25°F)	Fair	Fair	Good	Good	Good
Fluidity(100°F)	Good	Good	Good	Fair	Poor

These results show that there is an optimum range of oil content with this composition to have a product with good tack at 25°F and good structural integrity, or non-fluidity, at 100°F. The optimum oil amount range for this composition is from about 5 to 25 grams or from 2% to 8.5% by weight, or preferably 15 to 25 grams or 12.8% to 21.1% by weight.

### Example IV

30 The following example shows the results of varying the mole ratio of polyol to isocyanate.

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Asphalt	73.8 gr	73.8	73.8	73.8
Oil	11.4	11.4	11.4	11.4
35 CaCO <sub>3</sub>	14.8	14.8	14.8	14.8
Poly BD®	15.0	15.0	15.0	15.0
Isocyanate	1.88	1.6	1.3	1.1
Catalyst	0.1	0.1	0.1	0.1
40 Equiv Ratio (ISO/Poly-BD)	1.0	0.85	0.72	0.6

As the level of isocyanate is decreased, the tack increases at 25°F, but 100°F fluidity suffers when the equivalent ratio drops below 0.85. The optimum range of

Poly-BD® in this composition is about 25 to 10 or preferably 20 to 10 with isocyanate about 3.0 to 1.0 or preferably 2.5 to 1.25.

Example V

- 5 This series shows the effect of varying the amount of urethane in the composition.

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Asphalt.	73.8 gr	73.8	73.8	73.8
Oil	11.4	11.4	11.4	11.4
10 CaCO <sub>3</sub>	14.8	14.8	14.8	14.8
Poly BD®	30.0	15.0	6.0	3.0
Isocyanate	3.76	1.88	0.75	0.37
Catalyst	0.1	0.1	0.1	0.1

- Sample A built too much strength and reduced the tack.
- 15 Samples C and D did not build enough strength to make a viable product. Sample B produced a tacky product with good cold tack and good 100°F fluidity. This composition employed a constant amount of oil. The composition can be used without any oil, but oil additive is preferred as a
- 20 tackifier to provide the proper balance between structural integrity (stiffness) given by the urethane polymer with some tackiness, and an increased level of tackiness with structural integrity over the desired temperature range. Therefore, the amount of urethane can vary from about 3 to
- 25 30 grams in this composition if the amount of oil is also adjusted; however, high amounts of urethane polymer are limited by cost factors.

## CLAIMS

What is claimed is:

2      **Claim 1.** A urethane-modified bitumen sheet material  
adapted for use as a moisture barrier, which sheet material  
comprises:

- 4            a) a bitumen layer which comprises bitumen and a  
minor modifying amount of a urethane polymer to impart  
6            stable, non-flow properties and a selected degree of  
surface tackiness to the bitumen layer in use, the  
8            urethane polymer prepared by the reaction of a  
polyisocyanate with a long-chain polydiene hydrocarbon  
10           with terminal groups which react with the  
polyisocyanate to form a urethane polymer;  
12           b) an outer polymer film bonded to one surface of the  
bitumen layer; and  
14           c) a releasable film bonded to the other surface of  
the bitumen layer, which releasable film is subject to  
16           removal prior to use of the sheet material to expose a  
tacky surface of the bitumen layer for application of  
18           the tacky surface to the surface to be protected.

2      **Claim 2.** The sheet material of claim 1 wherein the  
bitumen layer comprises from about 2% to 30% by weight of  
the urethane polymer.

2      **Claim 3.** The sheet material of claim 1 wherein the  
polydiene hydrocarbon comprises a hydroxyl-terminated  
polybutadiene homopolymer.

2      **Claim 4.** The sheet material of claim 1 wherein the  
bitumen layer includes a filler material in an amount of  
from about 5% to 40% by weight of the bitumen layer.

2      **Claim 5.** The sheet material of claim 1 wherein  
polyisocyanate comprises a diphenyl methane 4,4'<sup>1</sup>  
diisocyanate.

2      **Claim 6.** The sheet material of claim 1 wherein the  
outer polymer film comprises an olefinic polymer film which  
is heat resistant at about temperatures above 160°F.



Claim 7. The sheet material of claim 1 wherein the  
2 outer polymer film comprises a cross-linked, low density  
polyethylene film.

Claim 8. The sheet material of claim 1 wherein the  
2 releasable film comprises a release paper having a release  
surface.

Claim 9. The sheet material of claim 1 wherein the  
2 bitumen layer comprises a urethane polymer derived from a  
reaction of an aromatic diisocyanate in the presence of a  
4 curing agent and long-chain polydiene hydrocarbon having  
primary terminal hydroxyl groups, with a hydroxyl  
6 functionality ranging from about 2.2 to 2.6.

Claim 10. The sheet material of claim 1 wherein the  
2 bitumen layer ranges from about 20 to 150 mils in thickness,  
and the outer film and the releasable film range from about  
4 1 to 10 mils in thickness.

Claim 11. The sheet material of claim 1 wherein the  
2 bitumen layer exhibits surface tackiness and non-flow stable  
properties over the range of about 10°F to 125°F.

Claim 12. The sheet material of claim 1 wherein the  
2 bitumen layer includes a tackifier agent in an amount  
sufficient to impart selected surface tackiness to the  
4 bitumen layer.

Claim 13. The sheet material of claim 12 wherein the  
2 tackifier agent comprises a mineral hydrocarbon oil.

Claim 14. The sheet material of claim 13 wherein the  
2 mineral hydrocarbon oil is present in an amount of about 5%  
to 25% by weight of the bitumen layer.

Claim 15. In combination, a concrete structure which  
2 includes a tacky surface of the sheet material of claim 1  
secured to the wall of the concrete structure and with the  
4 releasable film sheet removed from the sheet material.

Claim 16. A modified, urethane bitumen sheet material  
2 adapted for use as a moisture barrier for masonry, which  
sheet material comprises:

4 a) a bitumen layer which comprises bitumen, a filler  
material, a mineral oil tackifier agent and an amount

6 of about 2% to 30% by weight of the bitumen layer of a  
urethane polymer to impart desirable non-flow  
8 properties and a selected degree of surface tackiness  
to the bitumen layer in use over a temperature range of  
10 about 25°F to 100°F, the urethane polymer prepared by  
the reaction in the presence of a curing agent of an  
12 aromatic diisocyanate with a long-chain polybutadiene  
hydrocarbon with hydroxyl terminal groups to form a  
14 urethane polymer;  
b) a thin, outer, cross-linked, olefin, polymer film  
16 bonded to one surface of the bitumen layer; and  
c) a releasable paper on the other surface of the  
18 bitumen layer, which releasable paper is subject to  
removal prior to use of the sheet material to expose a  
20 tackified surface of the bitumen layer for application  
of the tackified surface to the surface of the masonry  
22 to be protected.

**Claim 17.** A method of preparing a urethane-modified  
~~2 bitumen sheet material adapted for use as a moisture~~  
barrier, which method comprises:

4 a) preparing a hot, melted bitumen composition which  
comprises bitumen and a minor modifying amount of a  
6 urethane polymer, which urethane polymer is prepared by  
the reaction of a polyisocyanate with a long-chain  
8 polydiene hydrocarbon having terminal groups which  
react with the polyisocyanate to form the urethane  
10 polymer;  
b) applying a layer of the melted bitumen composition  
12 onto a releasable film, which film may be easily  
removed from the cooled surface of the bitumen layer  
14 prior to use;  
c) applying an outer polymeric film to an exposed  
16 surface of the bitumen layer to bond the outer  
polymeric film to the bitumen layer;  
18 d) cooling the bitumen layer; and  
e) recovering the sheet material for use as a  
20 moisture barrier sheet material.

Claim 18. The method of claim 17 wherein the polymeric  
2 film comprises a cross-linked, low density olefinic film.

Claim 19. The method of claim 17 wherein the releasable  
2 film comprises a paper with a releasable surface.

Claim 20. The method of claim 17 which includes adding  
2 the polyisocyanate and the hydrocarbon to a mixing vessel  
containing the hot bitumen and carrying out the reaction in  
4 the mixing vessel.

Claim 21. The method of claim 17 wherein the  
2 hydrocarbon comprises a hydroxyl-terminated polybutadiene  
and the polyisocyanate comprises an aromatic diisocyanate.

Claim 22. The sheet material produced by the method of  
2 claim 17.

Claim 23. The method of claim 17 wherein the bitumen  
2 composition includes a filler material.

Claim 24. The method of claim 17 wherein the bitumen  
2 composition includes a tackifier agent in an amount to  
impart a selected tackiness to the surface of the bitumen  
4 layer.

Claim 25. The method of claim 24 wherein the tackifier  
2 agent comprises a hydrocarbon oil in an amount of about 5%  
to 30% by weight of the bitumen composition.

Claim 26. The method of claim 24 which includes  
2 separately introducing heated bitumen, the polyisocyanate  
and the long-chain polydiene hydrocarbon into an injection  
4 nozzle for *in situ* reaction and mixing, and injecting the  
melted, urethane-bitumen composition onto the releasable  
6 film supported on a conveyor belt.

Claim 27. A method of providing a moisture barrier to  
2 a surface, which method comprises:

- a) removing the releasable film of the sheet material  
4 of claim 1; and
- b) applying the tacky, exposed surface of the bitumen  
6 layer to the surface to be protected.

Claim 28. The method of claim 27 wherein the surface to  
2 be protected comprises a poured concrete wall surface.

2       **Claim 29.** The protected wall surface prepared by the  
2 method of claim 27.

2       **Claim 30.**       A polymer-modified bitumen coating  
2 composition adapted for use as a moisture-barrier coating  
layer, which composition comprises:

4       a) bitumen;

6       b) a modifying amount of a urethane polymer prepared by  
the reaction of a polyisocyanate with a long chain,  
polydiene hydrocarbon with terminal groups which react with  
8 the polyisocyanate to form the urethane polymer;

10       c) a tackifier agent in sufficient amount to impart  
surface tackiness to the surface of the bitumen composition;

12       d) a minor amount of a particulate filler material; and

14       e) the bitumen composition characterized by as selected  
degree of surface tackiness and stable fluid properties over  
a temperature range of about 10 to 120 degrees Fahrenheit.

2       **Claim 31.** The composition of claim 20 wherein the  
polydiene hydrocarbon comprises a hydroxyl-terminated  
polybutadiene.

2       **Claim 32.** The composition of claim 30 wherein the  
filler material comprises from about 5 to 50 percent by  
weight of the composition.

2       **Claim 33.** The composition of claim 30 wherein the  
filler material comprises calcium carbonate having an  
average particle size of less than about 20 microns.

2       **Claim 34.** The composition of claim 30 wherein the  
urethane polymer comprises from about 2 to 30 percent by  
weight of the composition.

2       **Claim 35.** The composition of claim 30 wherein the  
tackifier agent comprises a mineral oil.

2       **Claim 36.** The composition of claim 35 wherein the  
tackifier agent comprises from about 5 to 25 percent by  
weight of the composition.

2       **Claim 37.** The composition of claim 30 wherein the  
composition is characterized by a stable non-fluid property  
in a vertical position over a temperature range of about 20  
4 to 100 degrees F.

Claim 38. A coating layer of the composition of claim  
2 30 which has a thickness of about 20 to 150 mils.

Claim 39. The composition of claim 30 wherein the  
2 bitumen comprises a propane deactivated bitumen.

Claim 40. The composition of claim 30 wherein the  
2 reaction occurs *in situ* at a coating applicator.

## AMENDED CLAIMS

[received by the International Bureau on 8 November 1996 (08.11.96);  
original claims 1, 5, 10-12 and 15-17 amended;  
remaining claims unchanged (5 pages)]

- Claim 1.** A urethane-modified bitumen sheet material  
2 adapted for use as a moisture barrier, which sheet material  
comprises:  
4 a) a bitumen layer which comprises bitumen and a minor  
modifying amount of a urethane polymer to impart stable, non-  
6 flow properties and surface tackiness properties to the  
bitumen layer in use over a range of about 10°F to 125°F, the  
8 urethane polymer prepared by the reaction of a polyisocyanate  
with a long-chain polydiene hydrocarbon with terminal groups  
10 which react with the polyisocyanate to form a urethane  
polymer;  
12 b) an outer polymer film bonded to one surface of the  
bitumen layer; and  
14 c) a releasable film bonded to the other surface of the  
bitumen layer, which releasable film is subject to removal  
16 prior to use of the sheet material to expose a tacky surface  
of the bitumen layer for application of the tacky surface to  
18 the surface to be protected.

**Claim 2.** The sheet material of claim 1 wherein the  
2 bitumen layer comprises from about 2% to 30% by weight of the  
urethane polymer.

**Claim 3.** The sheet material of claim 1 wherein the  
2 polydiene hydrocarbon comprises a hydroxyl-terminated  
polybutadiene homopolymer.

**Claim 4.** The sheet material of claim 1 wherein the  
2 bitumen layer includes a filler material in an amount of from  
about 5% to 40% by weight of the bitumen layer.

**Claim 5.** The sheet material of claim 1 wherein  
2 polyisocyanate comprises a diphenyl methane diisocyanate.

**Claim 6.** The sheet material of claim 1 wherein the  
2 outer polymer film comprises an olefinic polymer film which  
is heat resistant at about temperatures above 160°F.

**Claim 7.** The sheet material of claim 1 wherein the  
2 outer polymer film comprises a cross-linked, low density  
polyethylene film.

Claim 8. The sheet material of claim 1 wherein the  
2 releasable film comprises a release paper having a release  
surface.

Claim 9. The sheet material of claim 1 wherein the  
2 bitumen layer comprises a urethane polymer derived from a  
reaction of an aromatic diisocyanate in the presence of a  
4 curing agent and long-chain polydiene hydrocarbon having  
primary terminal hydroxyl groups, with a hydroxyl  
6 functionality ranging from about 2.2 to 2.6.

Claim 10. The sheet material of claim 1 wherein the  
2 bitumen layer ranges from about 20 to 150 mils in thickness,  
and the outer film and the releasable film each range from  
4 about 1 to 10 mils in thickness.

Claim 11. The sheet material of claim 1 wherein the  
2 bitumen layer exhibits surface tackiness and non-flow stable  
properties over the range of about 25°F to 100°F.

Claim 12. The sheet material of claim 1 wherein the  
2 bitumen layer includes a tackifier agent in an amount to  
impart additional surface tackiness to the bitumen layer.

Claim 13. The sheet material of claim 12 wherein the  
2 tackifier agent comprises a mineral hydrocarbon oil.

Claim 14. The sheet material of claim 13 wherein the  
2 mineral hydrocarbon oil is present in an amount of about 5%  
to 25% by weight of the bitumen layer.

Claim 15. In combination, a concrete structure having  
2 a wall surface which includes a tacky exposed surface of the  
sheet material of claim 1 secured to the wall surface of the  
4 concrete structure and with the releasable film sheet removed  
from the sheet material.

Claim 16. A modified, urethane bitumen sheet material  
2 adapted for use as a moisture barrier for masonry, which  
sheet material comprises:

4 a) a bitumen layer which comprises bitumen, a filler  
material, a mineral oil tackifier agent and an amount of  
6 about 2% to 30% by weight of the bitumen layer of a urethane  
polymer to impart desirable non-flow properties and desirable  
8 surface tackiness to the bitumen layer in use over a  
temperature range of about 25°F to 100°F, the urethane

10 polymer prepared by the reaction in the presence of a curing  
agent of an aromatic diisocyanate with a long-chain  
12 polybutadiene hydrocarbon with hydroxyl terminal groups to  
form a urethane polymer;

14 b) a thin, outer, cross-linked, olefinic, polymer film  
bonded to one surface of the bitumen layer; and

16 c) a releasable paper on the other surface of the  
bitumen layer, which releasable paper is subject to removal  
18 prior to use of the sheet material to expose a tackified  
surface of the bitumen layer for application of the tackified  
20 surface to the surface of the masonry to be protected.

**Claim 17.** A method of preparing a urethane-modified  
2 bitumen sheet material adapted for use as a moisture barrier,  
which method comprises:

4 a) preparing a hot, melted bitumen composition which  
comprises bitumen and a minor modifying amount of a urethane  
6 polymer, which urethane polymer is prepared by the reaction  
~~of a polyisocyanate with a long-chain polydiene hydrocarbon~~  
8 having terminal groups which react with the polyisocyanate to  
form the urethane polymer to provide stable, non-flow  
10 properties and surface tackiness properties to the bitumen  
layer over the range of about 10°F to 125°F;

12 b) applying a layer of the melted bitumen composition  
onto a releasable film, which film may be easily removed from  
14 the cooled surface of the bitumen layer prior to use;

c) applying an outer polymeric film to an exposed  
16 surface of the bitumen layer to bond the outer polymeric film  
to the bitumen layer;

18 d) cooling the bitumen layer; and

e) recovering the sheet material for use as a moisture  
20 barrier sheet material.

**Claim 18.** The method of claim 17 wherein the polymeric  
2 film comprises a cross-linked, low density olefinic film.

**Claim 19.** The method of claim 17 wherein the releasable  
2 film comprises a paper with a releasable surface.

**Claim 20.** The method of claim 17 which includes adding  
2 the polyisocyanate and the hydrocarbon to a mixing vessel



containing the hot bitumen and carrying out the reaction in  
4 the mixing vessel.

**Claim 21.** The method of claim 17 wherein the  
2 hydrocarbon comprises a hydroxyl-terminated polybutadiene and  
the polyisocyanate comprises an aromatic diisocyanate.

**Claim 22.** The sheet material produced by the method of  
2 claim 17.

**Claim 23.** The method of claim 17 wherein the bitumen  
2 composition includes a filler material.

**Claim 24.** The method of claim 17 wherein the bitumen  
2 composition includes a tackifier agent in an amount to impart  
a selected tackiness to the surface of the bitumen layer.

**Claim 25.** The method of claim 24 wherein the tackifier  
2 agent comprises a hydrocarbon oil in an amount of about 5% to  
30% by weight of the bitumen composition.

**Claim 26.** The method of claim 24 which includes  
2 separately introducing heated bitumen, the polyisocyanate and  
the long-chain polydiene hydrocarbon into an injection nozzle  
4 for *in situ* reaction and mixing, and injecting the melted,  
urethane-bitumen composition onto the releasable film  
6 supported on a conveyor belt.

**Claim 27.** A method of providing a moisture barrier to  
2 a surface, which method comprises:

- 4 a) removing the releasable film of the sheet material  
of claim 1; and
- 6 b) applying the tacky, exposed surface of the bitumen  
layer to the surface to be protected.

**Claim 28.** The method of claim 27 wherein the surface to  
2 be protected comprises a poured concrete wall surface.

**Claim 29.** The protected wall surface prepared by the  
2 method of claim 27.

**Claim 30.** A polymer-modified bitumen coating  
2 composition adapted for use as a moisture-barrier coating  
layer, which composition comprises:

- 4 a) bitumen;
- 6 b) a modifying amount of a urethane polymer prepared by  
the reaction of a polyisocyanate with a long chain, polydiene

hydrocarbon with terminal groups which react with the  
8 polyisocyanate to form the urethane polymer;

c) a tackifier agent in sufficient amount to impart  
10 surface tackiness to the surface of the bitumen composition;

d) a minor amount of a particulate filler material; and

12 e) the bitumen composition characterized by as selected  
degree of surface tackiness and stable fluid properties over  
14 a temperature range of about 10 to 120 degrees Fahrenheit.

Claim 31. The composition of claim 20 wherein the  
2 polydiene hydrocarbon comprises a hydroxyl-terminated  
polybutadiene.

Claim 32. The composition of claim 30 wherein the  
2 filler material comprises from about 5 to 50 percent by  
weight of the composition.

Claim 33. The composition of claim 30 wherein the  
2 filler material comprises calcium carbonate having an average  
particle size of less than about 20 microns.

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Claim 34. The composition of claim 30 wherein the  
2 urethane polymer comprises from about 2 to 30 percent by  
weight of the composition.

Claim 35. The composition of claim 30 wherein the  
2 tackifier agent comprises a mineral oil.

Claim 36. The composition of claim 35 wherein the  
2 tackifier agent comprises from about 5 to 25 percent by  
weight of the composition.

Claim 37. The composition of claim 30 wherein the  
2 composition is characterized by a stable non-fluid property  
in a vertical position over a temperature range of about 20  
4 to 100 degrees F.

Claim 38. A coating layer of the composition of claim  
2 30 which has a thickness of about 20 to 150 mils.

Claim 39. The composition of claim 30 wherein the  
2 bitumen comprises a propane deactivated bitumen.

Claim 40. The composition of claim 30 wherein the  
2 reaction occurs *in situ* at a coating applicator.

STATEMENT UNDER ARTICLE 19

The amendments made to the claims are to correct grammatical and typographical errors, and to more clearly and completely define Applicant's contribution to the art. No new matter has been added and therefore the amended claims have no impact on the description and drawings. Pages 14-18 have been substituted to replace original claim pages 14-19.

Acceptance of these amendments is respectfully requested.

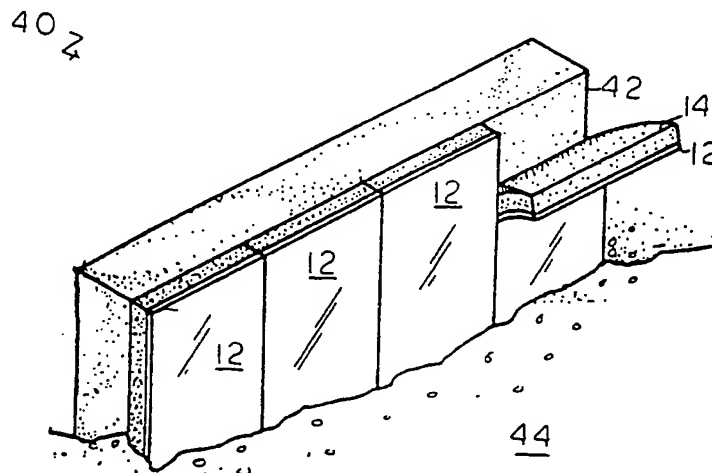
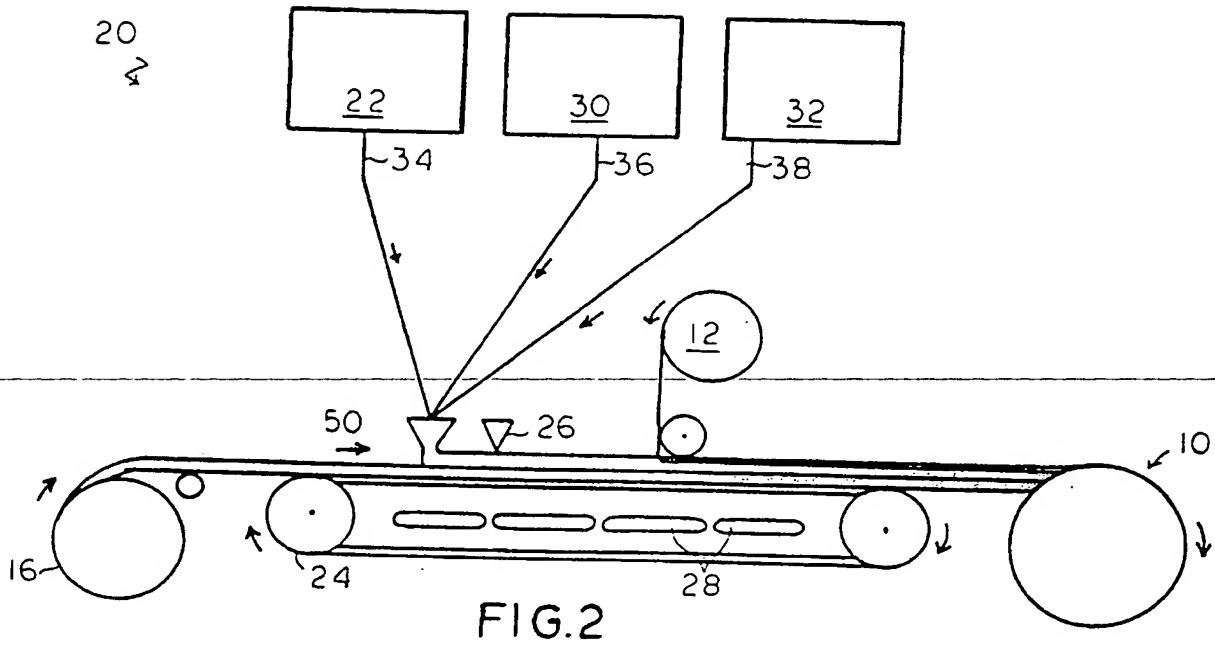
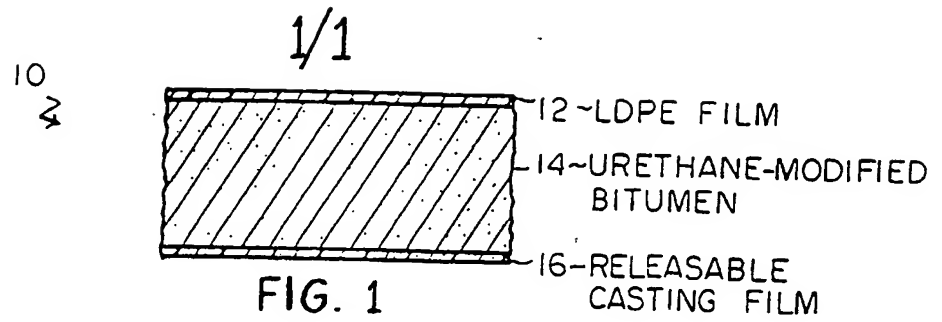


FIG. 3  
SUBSTITUTE SHEET (RULE 26)

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US96/11446

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : 52/169.14; 428/40.3, 41.7, 41.8, 491; 524/59

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 52/169.14; 428/40.1, 40.3, 41.7, 41.8, 491; 524/59

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	MIRADRI Sales Brochure, Nicolon Corp. Norcross, Georgia USA, Sweet's General Building & Renovation 1995 Catalog, "Self-Adhered Waterproofing From the Drainage Experts", pages 2-4.	1-29
Y	US, A, 4,871,792 (LUCKE) 03 October 1989, col. 2, lines 7-18, col. 6, lines 19-53, and col. 8, lines 4-8.	1-2, 4-5, 13-14, 16, 20, 23-25, and 30-40
Y	Poly BD Resins in Urethane Elastomers, ARCO Chemical Company product bulletin, 1994, pages 2-4 and 19.	2-3, 5, 9, 21, and 31

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

16 AUGUST 1996

Date of mailing of the international search report

13 SEP 1996

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Form PCT/ISA/210 (second sheet)(July 1992)\*



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/11446

## A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

E02D 19/00; E04F 13/00; D21H 19/24; D06N 5/00; C08L 95/00; B32B 11/06

